Response To "Kinetic And Mechanistic Studies Of The Recombination Of Oh With No2: Vibrational Deactivation, Isotopic Scrambling And Product Isomer Branching Ratios"

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General Discussion

Professor Stutz opened the discussion of Professor Ravishankara's paper: How much of the fast temporal variability, for example of NO_3 and N_2O_5, is due to meteorology and not chemistry?

Professor Ravishankara replied: Clearly, both meteorology–dynamics and chemistry play roles in the temporal (and spatial) variability of species that one sees in the atmosphere. In case of NO_3 and N_2O_5, the emission, the chemical transformations, the removal (deposition) and transport all play critical roles. Yes, one could have variability only due to meteorology (*à la* transport) for a while. However, if there are no chemical processes that interconvert and remove species such as NO_3 and N_2O_5, the variability will decrease, and eventually will be negligible. In my opinion, the combination of meteorology and chemistry and their synergistic, or opposing actions, define the extent of the variability. Lastly, I wonder if it is beneficial to even separate the "factors". In a way, the answer to your question (the way I read it) may depend on the order in which you add (or take away) the one of the two factors.

I believe that one can think along the same lines even for the high frequency variations.

Professor Pyle asked: Why, given an apparently large difference in the individual terms in the tropospheric ozone budget, do models seem to always get the 'right' answer?

Professor Ravishankara responded: As you know, I am really an experimentalist! Prof. Pyle can answer his own question much better than me!

My suspicion is that the models are tweaked and some times even constrained (for example to get the mass balance) so that the tropospheric budget works out. I think that you can see it in the model results I showed. Of course, if they did not balance production with removal, we would have a steady large build up or decline in ozone. I personally believe that deposition is one of the ill-defined, parameterized, processes; we really should try to understand the details and constrain this removal process.

Dr Tuck commented: I believe that Prof. Ravishankara is right to emphasize the importance of variability. It is becoming apparent that scale invariance is present in observations of adequate resolution, quality and range of scales; it implies the occurrence of skewed probability distribution functions with fat tails. While this is probably not what current models produce in an adequate way, the good news is that a simple scaling exponent can generate statistically representative variability over a range of scales, thus enabling in principle a low cost parameterization for model sub-grid scales.

Professor Ravishankara answered: I agree with Dr Tuck's analysis. I would only add that we would be better served if we took advantage of the variability to understand the system and also figure out how the atmosphere "integrates" the variability. The latter, to me, is a very interesting issue.

Dr Evans asked: Given the variability of atmospheric composition seen on all spatial and temporal scales, why are models capable of resolving much of what is occurring within the atmosphere?

Professor Ravishankara replied: I am not sure that the models really resolve all such variability. I do not believe that the resolutions of the models are really high enough to define the variability on

time scales of seconds and spatial scales of metres. Even if they were, do they represent all the highly varying processes? Yet, I think that Dr Evans has a point. I think that the atmosphere integrates some of the variability (please see my answer to Dr Tuck's question) and "helps" us in some ways.

Professor Herrmann remarked: It should be noted that not only the nature of cloud condensation nuclei (CCN) influences cloud droplet formation but that also in turn clouds do process and chemically modify particles changing their CCN properties.

Professor Ravishankara said: I agree! I did not bring up the issue of aerosol processing by clouds in my talk. Professor Herrmann is right in highlighting this process. Once a good CCN, always a good CCN? I wonder! Once the aerosol activated a droplet formation, would it be capable (better capable?) of activating again? There is much to be learned in this area.

Dr Chipperfield opened the discussion of Professor Pyle's paper: Please note that an updated version of the SLIMCAT CTM does now give a good simulation of Arctic ozone loss and therefore captures the slope of the plot of ozone loss against polar stratospheric cloud (PSC) volume (V_{PSC}). The improvements in the CTM to achieve this include updates to the kinetics, a NAT-based denitrification scheme and improvements in the modelled diabatic descent in the vortex. This work is published in Chipperfield et al.[1]

For the authors' simplified chemistry scheme they impose a rate of O_3 loss based on SH observations. Therefore, the reason why they do not reproduce the slope must be due to some other factor than an underestimation of the chemical loss rate. Can you comment on this?

It is interesting that the model appears to give a compact correlation. Although full chemistry models, which may have more 'non-linear' processes also seem to do this, it is still somewhat surprising in both cases. It may be that as sunlight is needed for both O_3 loss and deactivation there is a compensation of the rate of these two processes and hence some limit on the O_3 loss which can be obtained. Can the authors see anything in their specified rate of O_3 loss and cold tracer deactivation which may lead to such a compensation?

1 M. P. Chipperfield, W. Feng, and M. Rex. *Geophys. Res. Lett.*, 2005, **32**(11), L11813, DOI: 10.1029/2005GL022674.

Professor Pyle responded: We do explicitly acknowledge in our paper the fact that newer versions of SLIMCAT can reproduce the observed slope. However, based on ref. 1 it is not possible to diagnose explicitly a single cause of that improvement.

The *in situ* chemical loss rate is not the only thing determining the ozone loss over NH winter. In addition the position of the vortex, in particular daylight hours experienced by an air parcel that previously had experienced temperatures below T_{NAT} is contributing as well to the loss rate accumulated over a winter period ("processing efficiency").

1 W. Feng, M. P. Chipperfield, S. Davies, B. Sen, G. Toon, J. F. Blavier, C. R. Webster, C. M. Volk, A. Ulanovsky, F. Ravegnani, P. von der Gathen, H. Jost, E. C. Richard and H. Claude, *Atmos. Chem. Phys.*, 2005, **5**, 139–152.

We also think that it is interesting that the model reproduces a compact relationship. However, the careful reader will see that have not given an explanation! We do think that the spatial/temporal averaging inherent in producing the plot probably removes much of the non-linearity. However, we acknowledge that further work is required to explore this.

Professor Pyle then asked: In your improved relationship between V_{PSC} and ozone loss, how much is due to changing descent in the SLIMCAT model?

Dr Chipperfield replied: The new model results which show much better agreement with observations of polar ozone loss are discussed in Chipperfield et al.[1] (see their Fig. 1). The improvements in the model calculations are the result of a number of complementary factors which all make a contribution. Some of these will apply to all models and some are specific to our

CTM. The computational cost of the model runs precluded a step-by-step inclusion of all of these changes in a series of long model runs.

The new simulation included updates to ClO/Cl_2O_2 kinetics which result in faster loss due to one of the principal polar O_3 loss cycles, though this effect is expected to be comparatively small. The model also now has a treatment of denitrification by large NAT particles which allows the model to denitrify during the cold years of e.g. 1995, 1996 and 1997 which did not happen using the previous ice-based scheme. Davies et al.[2] showed that in the cold winter of 1999/2000 this increased modelled O_3 loss by about 30%, which is probably an upper limit for this effect. The transport in our CTM has been improved by the change from the former MIDRAD radiation scheme to the CCM scheme now that SLIMCAT extends down to the surface. This change in radiation scheme results in stronger modelled polar winter descent and more inorganic chlorine (Cl_y) in the lower stratosphere available for activation (see Feng et al.,[3]). This model-specific change is likely to be a significant factor in the improvement, and is supported by the changed profile of O_3 loss in the lower stratosphere in 1996 in Fig. 2 of ref. 1. We should also note that the source gas scenario used to force the new model runs has an extra 100 pptv of stratospheric Cl_y assumed to come from shorter lived Cl source gases.[4] This will increase polar lower stratosphere Cl_y by about 3%.

So, overall the change in modelled descent is an important factor but it is important to understand that it is affecting the modeled O_3 loss through increased Cl_y. We diagnose O_3 loss directly (using a passive tracer) and so this sensitivity is not physically the same as that where diagnosing O_3 loss indirectly from by reconstructing the O_3 transport terms depends on what is taken for the vertical winds and horizontal mixing.

1 M. P. Chipperfield, W. Feng, and M. Rex. *Geophys. Res. Lett.*, 2005, **32**(11), L11813, DOI: 10.1029/2005GL022674.
2 S. Davies, M. P. Chipperfield, K. S. Carslaw, B.-M. Sinnhuber, J. G. Anderson, R. M. Stimpfle, D. M. Wilmouth, D. W. Fahey, P. J. Popp, E. C. Richard, P. von der Gathen, H. Jost and C. R. Webster, *J. Geophys. Res.*, 2002, **107**, DOI: 10.1029/2001JD000445.
3 W. Feng, M. P. Chipperfield, S. Davies, B. Sen, G. Toon, J. F. Blavier, C. R. Webster, C. M. Volk, A. Ulanovsky, F. Ravegnani, P. von der Gathen, H. Jost, E. C. Richard and H. Claude, *Atmos. Chem. Phys.*, 2005, **5**, 139–152.
4 World Meteorological Organization, *Scientific Assessment of Ozone Depletion: 2002*, Global Ozone Research and Monitoring Project, Report No. 47, Geneva, 2003

Professor Zellner observed: The correlations between column ozone change and total PSC volume are based on HNO_3/H_2O fields and NAT threshold temperatures. Since there exists various types of PSCs that have different threshold temperatures and different halogen activation behaviours, temperature variability during PSC formation and PSC existence might be very important.

Dr Chipperfield replied: There are indeed many processes related to polar ozone loss which are expected to be non-linear and show 'threshold' behaviour. For this reason it is remarkable that the observations of column O_3 loss does show such a compact and linear correlation with cold temperatures, when averaged over certain regions. Although models do seem to show a similar behaviour the reason(s) for this apparently compact linear correlation (*i.e.* lack of non-linearity) have not been established.

Dr H. Roscoe addressed Professor Pyle:

(1) Hopefully, this modelling work will soon use equivalent-latitude means of quantities in the polar stratosphere rather than the zonal means in the paper.

(2) Mean zonal wind is a confusing measure of vortex strength, particularly in the Arctic. We know that the mean meridional wind is ≤ 0.5 m s^{-1}, from age-of-air studies, so the wind speed ($\sqrt{u^2 + v^2}$) is the vortex wind, not the zonal wind (u). The danger is that some correlations *vs.* zonal wind in the paper may be self-fulfilling because zonal wind is a measure of vortex eccentricity not of strength, *e.g.* small zonal wind must give a warmer vortex because the increased eccentricity leads to more sunlight on the vortex.
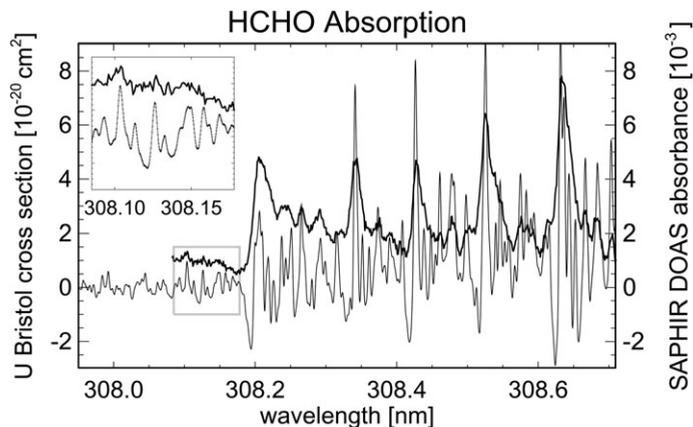
HCHO Absorption

Fig. 1 Comparison of the absorption spectrum of Pope *et al.* (2005) (thick line, left axis) and the HR DOAS absorbance measured in the SAPHIR chamber (thin line, right axis; see text for details). The inset denotes the spectral range where HCHO lines strongly overlap with the OH $Q_1(3)$, $Q_{21}(3)$, and $P_1(1)$ lines.

Professor Pyle replied:

(1) Zonal means and equivalent-latitude means are equally relevant and important quantities. In the way we interpret our results, the use of equivalent latitude means wouldn't change anything.

(2) If we accept Dr Roscoe's meridional velocity limit, a reasonably weak vortex with $u = 20$ m s^{-1} would result in a vortex strength of 20.0016 m s^{-1}—this wouldn't change anything in any plot. Monthly and zonal mean zonal winds are a reasonable approximation of mean vortex strength. And of course everybody knows that mean temperatures and winds are not independent! In addition, for meridional tracer transport an eccentric vortex would be less efficient (even though absolute windspeeds might be reasonably high) than a pole-centric vortex (peeling). By the way, in an eccentric vortex the polar temperatures might be determined more by dynamics than radiation.

Dr Shallcross said: You have identified a number of teleconnections in your model analysis; are there chemical tracers other than ozone itself that may be used to test your hypotheses?

Professor Pyle replied: Certainly we would expect to see patterns in species other than ozone. We do see an ENSO signal, for example, in water vapour and long-lived tracers. We have not however explored the question of which would be the optimum measurements to make to test any hypotheses.

Professor Ravishankara addressed Dr Chipperfield:
(1) Please interpret the slope and intercept in your plot of column O_3 loss *vs.* V_{PSC}.
(2) Why do you think that it is a straight line?

Dr Chipperfield responded: Based on current understanding we expect chemical winter/spring ozone loss to require some period of cold temperatures to activate chlorine. Therefore, we would indeed expect the line in the plot to pass through the origin (*i.e.* intercept of zero). However, the plot shows a non-zero intercept, implying that some (small) O_3 loss happens in winters without PSC occurrence. Explanations for this, consistent with current understanding, could be:

• The V_{psc} diagnostic, based on large-scale analyses, misses mesoscale regions of cold temperatures which are critical in these warm winters.

• The threshold for formation of nitric acid trihydrate (NAT) used in the V_{psc} diagnostic misses temperatures just above the NAT point which may still lead to some activation on cold liquid aerosol.

• It is a measure of the uncertainty in the observations of V_{psc} and/or the O_3 loss.

• Some purely gas-phase chemistry—not requiring Cl activation—may make a small contribution at the end of the period (*i.e.* late March).

Taken at face value the slope of the line is a measure of increased chemical O_3 loss caused by colder temperatures causing larger and more extensive chlorine activation. It seems surprising that it is such a straight line (see Dr H. Roscoe's remarks).

Dr Cox said: The thought crossed my mind that the apparent linear relationship between PSC volume (measure of Cl activation) and ozone loss in N. Polar regions reflects a strong Bromine contribution to the chemical ozone loss through BrO + ClO reaction, in contrast to the quadratic dependence expected from ClO + ClO reaction.

Dr Chipperfield replied: Based on diagnostics of our CTM runs we do see that the reaction ClO + BrO makes a large (over 50%) contribution to Arctic O_3 loss (*e.g.* Chipperfield *et al.* 1993). Furthermore, the dependence of ozone loss due to the ClO + ClO is not quadratic in ClO_x ($=$ClO + $2Cl_2O_2$). Changing steady-state partitioning in the ClO : Cl_2O_2 ratio as $[ClO_x]$ changes means that the power of this dependence is nearer 1.5.[1] Even so, one would still expect some non-linearity and threshold effects in PSC occurrence and ozone loss. The apparent linearity of the plot of these averaged quantities has not been explained.

1 K. R. Searle, M. P. Chipperfield, S. Bekki and J. A. Pyle, *J. Geophys. Res.*, 1998, **103**, 25409–25416.

Dr Monks opened the discussion of Dr Stevenson's paper: I wondered if you had looked at the humidity change feedback into cloudiness and therefore the physical change to photolysis fluxes. One could imagine a situation where a wetter world could be more cloudy providing a negative feedback (below cloud) on your enhanced [OH]. In general, it strikes me that the cloudiness–photolysis rate physical feedback is not well understood or diagnosed.

Dr Stevenson replied: Changes in cloudiness are included in these simulations, but have not been analysed in detail. Changes in precipitation related to climate change (Fig. 4 of the paper) give a good indication of changes in clouds. This shows significant regional changes in clouds, but any global trend is not obvious. Photolysis rates in STOCHEM are linked to cloud distributions, and they will be affected by these changes, however, changes in cloudiness do not appear to be a major feedback.

Dr Arnold asked: How much does uncertainty in the stratosphere–troposphere exchange ozone flux impact conclusions regarding the emission-driven changes to ozone?

Dr Stevenson responded: Fig. 9 of the paper illustrates the relative roles of emissions change *versus* climate change for ozone over the next three decades, and indicates that climate change will modulate emissions-driven ozone changes at a significant level. There is significant uncertainty over how climate change will affect the influx of stratospheric ozone to the troposphere. In this study, there was no significant effect, but in a recent inter-comparison of nine models,[1] several showed increases in stratospheric input. In no case did the change overwhelm emissions-driven changes, but the overall feedback of climate change on ozone ranged from negative to positive, with the two competing feedbacks of water vapour (reducing ozone) and stratospheric input (generally increasing ozone). This area will require further study in order to reach a scientific consensus.

1 D. S. Stevenson, F. J. Dentener, M. Schultz, K. Ellingsen, T. van Noije, O. Wild, G. Zeng, M. Ammann, C. S. Atherton, N. Bell, D. J. Bergmann, I. Bey, T. Butler, J. Cofala, W. J. Collins, R. G. Derwent, R. M. Doherty, J. Drevet, H. Eskes, A. Fiore, M. Gauss, D. Hauglustaine, L. Horowitz, I. Isaksen, M. Krol, J. F. Lamarque, M. Lawrence, V. Montanaro, J. F. Müller, G. Pitari, M. J. Prather, J. Pyle, S. Rast, J. Rodriguez, M. Sanderson, N. Savage, D. Shindell, S. Strahan, K. Sudo and S. Szopa, "Multi-model ensemble simulations of present-day and near-future tropospheric ozone", *J. Geophys. Res.*, 2005, submitted.

Professor Heard commented: In the paper changes in hydroxyl radical concentration are ascribed to changes in the rate of reaction (R3) between electronically excited $O(^1D)$ atoms and water

vapour. Future changes in water vapour levels will therefore lead to changes in OH levels. However, as the rate of this reaction is given by $k[O^1D][H_2O]$, it is important that the rate of any other processes that remove $O(^1D)$ are properly incorporated into the model. In the troposphere, about 10% of $O(^1D)$ is removed by reaction with water vapour to form OH, with the remainder being mainly removed by the reactions:

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \text{ Rate coefficient } k(N_2)(T)$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \text{ Rate coefficient } k(O_2)(T)$$
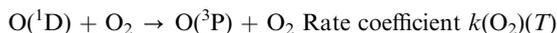
At higher altitudes, where there is less water vapour, these reactions become relatively more important for the removal of $O(^1D)$. It is not clear in the paper which value of $k(N_2)$ was used for the model calculations, and what the temperature dependence was? In a recent study, three independent laboratories, using two separate techniques, re-measured the value of $k(N_2)$ over a range of temperatures,[1–4] and at room temperature found a value $\sim$15% higher than previously recommended by IUPAC or NASA JPL. Depending on the value used in this paper, the level of hydroxyl radical calculated could be significantly different.

1   A. R. Ravishankara, E. J. Dunlea, M. A. Blitz, T. J. Dillon, D. E. Heard, M. J. Pilling, R. S. Strekowski, J. M. Nicovich and P. H. Wine, *Geophys. Res. Lett.*, 2002, **29**, DOI: 10.1029/2002GL014850.
2   M.A. Blitz, T. J. Dillon, D. E. Heard, M. J. Pilling and I. D. Trought, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2162–2171.
3   E. J. Dunlea and A. R. Ravishankara, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2152–2161.
4   R. S. Strekowski, J. M. Nicovich and P. H. Wine, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2145-2151.

Dr Stevenson responded: The rate coefficient used was:

$$k(N_2) = 1.8 \times 10^{-11} \, e^{(110/T)} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \text{ (where } T \text{ is temperature in } K).$$

This formula comes from the latest JPL evaluation.[1]

As a point of principle, we always use rate coefficients from the latest published data evaluations, because this is what they are for. We find it difficult to keep track of the chemical kinetics literature and to move with every nuance of the rate coefficient changes.

Of course, if this rate coefficient has increased by 15%, we would expect OH production *via* the $O(^1D) + H_2O$ route to have reduced by a similar amount. However, this is unlikely to result in a 15% reduction in [OH] as HO_x (OH + HO$_2$) is strongly buffered by a vast array of reactions. In addition, the rate coefficient for $O(^1D) + H_2O$ has also increased recently by a similar magnitude[2]— this may largely counteract any changes.

We look forward to full implementation of the latest set of recommendations for all rate coefficients with interest, and we will be eager to discover the overall impact of changes on our simulations of tropospheric chemistry.

1 http://jpldataeval.jpl.nasa.gov/
2 M. Pilling, personal communication.

Dr Chipperfield addressed Dr Stevenson and Professor Pyle: Your papers seem to give a different view of the importance of stratosphere–troposphere transport for the O_3 budget. Differences are certainly seen between different models but, as I understand it, these two models are both based on the Met Office Unified Model. Could the authors say how dynamically similar they expect their models to be and if they think the role of STE is consistent in their two versions?

Dr Stevenson replied: Firstly, see my response to Dr Arnold. The intercomparison study referred to in that response included both models. Both models are based upon the Met Office Unified Model (vn4.5 HadAM3), so their dynamics should behave in very similar ways. However, the two models treat their upper boundary (*i.e.* the lower stratosphere) rather differently. The STOCHEM model has its upper lid at about 100 hPa, and it generates a stratospheric influx of ozone at this level, based on an ozone climatology and the vertical winds at this level. The global

annual mean influx of stratospheric ozone is around 400 Tg (O_3) year^{-1} (Table 1 of the paper). The Cambridge model (UM_CAM) has its upper lid at 30 hPa, fixing ozone concentrations above that level to a climatology. Between 30 hPa and the tropopause, the model simulates chemistry and transport, as for the troposphere (*i.e.* with no explicit representation of stratospheric chemistry). This model finds a global annual mean influx of stratospheric ozone of around 600 Tg (O_3) year^{-1} (Stevenson *et al.*, submitted). In this large intercomparison, the mean (± 1 standard deviation) stratospheric influx across 19 models was 520 ± 200 Tg (O_3) year^{-1}, and this is also the approximate estimate and uncertainty derived from atmospheric observations (*e.g.* ref. 1). Both models can therefore be considered consistent with both other models and observations, and the differences between them can be understood in terms of the different treatments of the model upper boundary.

1 C. A. McLinden, S. C. Olsen, B. Hannegan, O. Wild, M. J. Prather, and J. Sundet, *J. Geophys. Res.*, 2000, **105**(D11), 14653–14666.

Professor Pyle also replied: The dynamical core is very similar, but the transport schemes are very different. Both models require assumptions/simplifications regarding the vertical ozone gradient above the tropopause. Even though the dynamical model should provide a similar "meteorology" for identical forcings (SSTs, CO_2) the response in the transport (in particular in convective areas) might be very different.

Dr Remedios said: It is clearly important to use sea surface temperature (SST) scenarios as proxies for climate change forcing over the next century. Your results, for example with respect to convection and isoprene, suggest that we should be considering land scenarios, such as land surface temperature changes and vegetation cover changes. Furthermore, the nature of convection and emissions would suggest that focus on particular regions of the land surface might prove particularly interesting. It would be very helpful if the authors of the two papers could comment on the prospects for such studies and whether they might place a different emphasis on any of the conclusions of their papers.

Dr Stevenson responded: Firstly, a point of clarification. Although we are driving our future climate using prescribed SSTs (and sea ice distributions) over the oceans (together with a prescribed change in the atmospheric concentration of radiatively active gases, such as CO_2), this does not mean that land temperatures remain fixed. The climate model version used had a land surface exchange scheme (MOSES2.2), and the land surface rapidly equilibrates with the imposed forcing. SSTs and sea-ice come from an earlier run of the coupled ocean-atmosphere version of the Hadley Centre model (HadCM3). We use SSTs simply to save computational effort, in terms of spin-up time and ocean modelling.

So the land temperatures used here are changing, and this is indeed important for biogenic emissions, and physical processes such as the distribution and intensity of convection. A separate modelling study has looked at possible future changes in vegetation, and the implications for isoprene emissions and ozone.[1] A further modelling study discusses the relationships between convection and isoprene emissions.[2]

1 M. G. Sanderson, C. D. Jones, W. J. Collins, C. E. Johnson and R. G. Derwent, *Geophys. Res. Lett.*, 2003, **30**(18), 1936, DOI: 10.1029/2003GL017642 .
2 R. M. Doherty, D. S. Stevenson, W. J. Collins and M. G. Sanderson, *Atmos. Chem. Phys. Discuss.*, 2005, **5**, 3747–3771.

Dr Cox asked: Were there any effects of precipitation changes on tropospheric ozone *e.g.* through changed deposition of relevant trace gases?

Dr Stevenson answered: We found no major global influence of changes in precipitation. Precipitation changes (Fig. 4 of the paper) are quite heterogeneous, and positive and negative regional effects may be tending to balance when globally averaged. Our confidence in regional climate change is much less than in global climate change; consequently we have not analysed regional changes in detail.

Professor Wayne opened a general discussion of Dr Stevenson and Professor Pyle's papers: I refer to the possibility that climate change could be mediated through chemical influences on water-vapour concentrations. Supersaturations and undersaturations suggest that the Clausius–Clapeyron equation is not always adequate for assessing P_{H_2O} in some regions. An obvious example, although very localized, is dehydration through PSC formation in the polar stratosphere in certain conditions. To what extent are chemical effects on P_{H_2O} dealt with in climate models? I believe that Dr Tuck has some apposite comments on these points.

Professor Pyle replied: Of course, water vapour is important for chemistry–climate connections. The most obvious example is the increase in water vapour calculated in a double-CO_2 atmosphere which has a tendency to reduce tropospheric ozone. Water is also important in the stratosphere where changes in the concentration of water in the lower stratosphere may well have impacted temperatures there. These processes have indeed been explored in climate models. The dehydration of the polar vortex may also have played a role (although I guess that the change in ozone is a bigger radiative factor there).

Dr Stevenson replied: I think this comment is mainly aimed at the stratosphere, which I will leave to Professor Pyle. Chemical effects on P_{H_2O} are essentially not represented in climate models (physical processes dominate the water budget)—the main exceptions are (i) oxidation of methane in the stratosphere, which provides an important source of water vapour; and (ii) *via* the second aerosol indirect effect, whereby aerosol changes the lifetime of cloud droplets.

Dr Tuck addressed Professor Wayne and Dr Chipperfield:

(1) The radiative cooling rates in the Antarctic vortex are significantly affected by removing water between 30 and 100 hPa in late June and July, as observed, and by removing ozone in September and October, again as observed.[1]

(2) The ozone loss in the stratospheric vortex would be better compared with simultaneous measurements of ozone and N_2O or CH_4, a technique which has strong recent support.[2–4] These are direct measurements, and even if intermittent, both from aircraft and satellites, constitute a test which to my knowledge no model has passed both in the Arctic and in Antarctica from the point of view of having the tracer amounts correct as a function of altitude in both vortices. The 'PSC volume' statistic contains model and analysis error in its temperature field and so is not really a true model comparison with observations.

1 J. Hicke and A. Tuck, *Q. J. Roy. Meteorol. Soc.*, 2001, **127**, 1645.
2 R. J. Salawitch, J. J. Margitan, B. Sen, G. C. Toon, G. B. Osterman, M. Rex, J. W. Elkins, E. A. Ray, F. L. Moore, D. F. Hurst, P. A. Romashkin, R. M. Bevilacqua, K. W. Hoppel, E. C. Richard and T. P. Bui. *J. Geophys. Res.*, 2002, **107** (D20), DOI: 10.1029/2001JD000620, Art. no. 8269.
3. M. H. Proffitt, K. Aikin, A. F. Tuck, J. J. Margitan, C. R. Webster, G. C. Toon, and J. W. Elkins. *J. Geophys. Res.*, 2003, **108** (D3), DOI: 10.1029/2002JD002657, Art. no. 4110.
4. F. Khosrawi, R. Müller, M. H. Proffitt, H. Nakajima, *J. Geophys. Res.*, 2004, **109**(D10301), DOI: 10.1029/2003JD004365.

Dr Chipperfield responded: Although we have not compared ozone loss diagnosed by tracer–tracer correlations we have compared the model directly with long-lived tracer data to test the model descent. Long-lived tracer comparisons from the recently updated SLIMCAT model, which shows the improved representation of polar ozone loss, are shown in ref. 1. In general the updated model appears to give a good representation of transport.

1. W. Feng, M. P. Chipperfield, S. Davies, B. Sen, G. Toon, J. F. Blavier, C. R. Webster, C. M. Volk, A. Ulanovsky, F. Ravegnani, P. von der Gathen, H. Jost, E. C. Richard and H. Claude, *Atmos. Chem. Phys.*, 2005, **5**, 139–152.

Dr Shallcross addressed Dr Stevenson: Once you start down the road of interactive models one must complete the cycle. First, if one changes the resolution of the vegetation model and therefore the resolution of the biogenic emissions grid does this significantly affect your conclusions about the

impact of isoprene? If the emission grid is finer it may be that isoprene destruction of ozone is more important. Second, if isoprene and related chemistry leads to elevated ozone will this not feedback on vegetation itself. It is known that vegetation is susceptible to ozone and it may well be that high ozone will retard vegetation growth and therefore isoprene emissions?

Dr Stevenson replied: The answer to the first question is not known, as we haven't carried out experiments varying resolution. It is quite possible that isoprene chemistry may be resolution dependent, as the outcomes for ozone of isoprene emissions strongly depend on the background NO_x levels. It will be interesting to see results from higher resolution models.

The second comment is also well made, but again this is a highly uncertain area. We know that very specific types of vegetation (*e.g.* oak trees) are major sources of isoprene, and that this isoprene is an important ozone precursor. We also know that ozone damages some types of vegetation (*e.g.*, wheat, soy-bean, *etc.*). However the detailed mechanisms of how these processes interact, and, for example their species dependence, is not well known. Earth system models are some way from simulating these sort of interactions in any detail.

Professor Cohen addressed Professor Pyle and Dr Chipperfield: How can we understand the effects of chemical variability as they feedback on meteorology? Is there an understanding of the mechanisms for feedback that would allow an estimate of the effects of chemical variability?

Professor Pyle replied: Although we concentrate here on the impact of climate variability on chemical composition (*e.g.*, the impact of ENSO on ozone fields) we do briefly mention the role of chemical change on meteorology (see the discussion about the variability of the southern hemisphere vortex and its connection to ozone, Fig. 2 of the paper). However, Prof Cohen does raise an important issue—there is a two-way feedback here.

Dr Chipperfield replied: In general the mechanisms by which chemistry feeds back onto meteorology is through radiation, *i.e.* chemistry changes the abundance of radiatively active gases. Chemistry may also change the distribution of clouds and aerosols, which also feeds back *via* radiation. Given good enough models, and enough computer resources, we could clearly do model experiments to assess the impact of modelled or prescribed variability. However, given the chaotic nature of the coupled system this would probably require large ensemble runs. From observations alone I think it is already a very difficult task to detect the feedbacks between large overall 'trend' signals. Isolating the impact of 'variability' from observations alone would require long, high quality datasets.

Dr Brauers opened the discussion of Professor Orr-Ewing's paper: Your HCHO absorption cross section data are a highly appreciated extension to existing data. The new data are compared to DOAS (differential optical absorption spectroscopy) measurements of HCHO with the instrument described by Hausmann *et al.*[1] predominantly used for OH detection. The linear dispersion is 0.24 pm pixel^{-1} and the current spectral resolution of 112000 corresponds to a resolution limit of 2.7 pm.

The Jülich HR DOAS spectrum was recorded in the SAPHIR (1) simulation chamber at 2.24 km light path, 6 ppb of HCHO, 301 K, and 998 hPa. The RMS noise in the DOAS spectra is 2×10^{-5}, at least 50 times less the observed signal. Our observations provide evidence that the fine structure of HCHO exhibits a pressure broadened line width in the order of 3 pm or less. This is less than the spectral resolution of the data provided by Pope *et al.* (2005).

1   M. Hausmann, U. Brandenburger, T. Brauers and H.-P. Dorn, *J. Geophys. Res.*, 1997, **102**, 16011.

Professor Orr-Ewing replied: We are pleased that our formaldehyde absorption cross section data are of value to those such as the Jülich group using DOAS for retrieval of atmospheric formaldehyde and OH mixing ratios. The disagreement between the spectra obtained using the instrument of Hausmann *et al.*[1] and our laser absorption spectrum is surprising, but we do not believe it is a consequence of the reduced resolution of the Bristol data presented in the figure of

Dr Brauers. We recently confirmed a bandwidth of the fundamental output of the dye laser used for our measurements of ≤ 0.12 cm^{-1} by recording and fitting laser induced fluorescence spectra of I$_2$ at wavelengths from 614–616 nm. Frequency doubling of this fundamental laser radiation should produce UV light at wavelengths around 308 nm with a bandwidth ≤ 0.17 cm^{-1} (≤ 1.6 pm in wavelength units). Fig. 2 shows absorption spectra of formaldehyde at wavelengths from 308–309.5 nm obtained in our apparatus at room temperature and low (~ 1 Torr) total pressure, using the methods described in our paper. One spectrum was recorded at an effective resolution of 0.01 nm (10 pm) but the second, higher resolution spectrum was obtained using the minimum step size of our dye laser, corresponding to 0.001 nm (1 pm). This latter spectrum is thus limited in resolution only by the laser bandwidth, which slightly exceeds the step size, and any homogeneous broadening of the spectral lines (Doppler broadening should add a heterogeneous Gaussian width to all spectral features of 0.07 cm^{-1} (0.7 pm)). Some additional structure is observed in the higher resolution spectrum, but not to the extent reported by Dr Brauers and coworkers. We would expect the effects of a pressure of ~ 1 atm of a bath gas such as air to add a further ~ 0.2 to 0.3 cm^{-1} of line broadening.[2]

The sharpest features we observe in the spectrum have estimated widths greater than 0.5 cm^{-1} corresponding to upper state lifetimes of ≤ 10 ps that are limited by rapid dissociation, consistent with our previous analysis of the $2_0^2 4_0^3$ and $2_0^3 4_0^1$ vibrational bands of the $\tilde{A}^1A_2$–$\tilde{X}^1A_1$ electronic transition in the wavelength range 313–320 nm.[2]

Finally, we note that the UV absorption spectrometer is not optimised for measurement of accurate absorption cross sections in the region of weak absorption from 308.0–308.2 nm, but that we have obtained further data in this region that might be of value for analysis of atmospheric DOAS measurements.

1   M. Hausmann, U. Brandenburger, T. Brauers and H.-P. Dorn, *J. Geophys. Res.*, 1997, **102**, 16011.
2   F. D. Pope, C. A. Smith, M. N. R. Ashfold and A. J. Orr-Ewing, *Phys. Chem. Chem. Phys.*, 2005, **7**, 79.

Dr Blitz commented: Our work on carbonyl photolysis—acetone, methyl ethyl ketone and diethyl ketone—indicates that barriers to products on the excited state exert a major influence on the quantum yields. Photolysis above the barrier tends to yield 100% photodissociation with little variation with pressure and temperature. However, below the barrier the excited state carbonyl has an extended lifetime and can be quenched back to the ground-state, and hence the quantum yield for photolysis much less than unity. Also, below the barrier the quantum yield shows a dramatic temperature dependence.

For example, the reciprocal photolysis yield *versus* pressure plots (Stern–Volmer plots) for acetone at 308 nm, a little below the barrier at 305 nm, show that the excited state is quenched with pressure and this effect dramatically increases as the temperature is lowered. These effects are even greater at longer wavelength, *i.e.* further below the barrier.

So using this idea of barriers to photodissociation in the excited state, when one looks at the formaldehyde data, bottom plot in Fig. 2, it can be seen that the quantum yield for photolysis starts to fall below 1.0 at wavelengths > 330 nm. This range is where I would expect the quantum yield to show an interesting *T*-dependence, and this is the information that is required by modellers. Why have Bristol concentrated their efforts studying formaldehyde at wavelengths below 330 nm? In addition, are there problems with the sensitivity of cavity ring-down spectroscopy in doing the experiments at wavelengths > 330 nm?

Professor Orr-Ewing said: In our view, the quantum yields for formaldehyde photochemistry over the entire wavelength region from 290–360 nm are of interest to tropospheric modellers, and we are thus steadily conducting experiments over this full range. It is our intention to measure the pressure and temperature dependent quantum yields for the H + HCO photolysis channel over as much of this wavelength range as time and resources permit. Recent activities have focused on short wavelengths because of the interest of the DOAS community in HCHO absorption cross sections around 308 nm (see the comment by Dr Brauers), but there are no technical reasons (such as CRDS sensitivity) why our experimental set-up cannot be used for measurements at wavelengths longer than 330 nm. Indeed, we expect the high resolution of our UV excitation to become more important
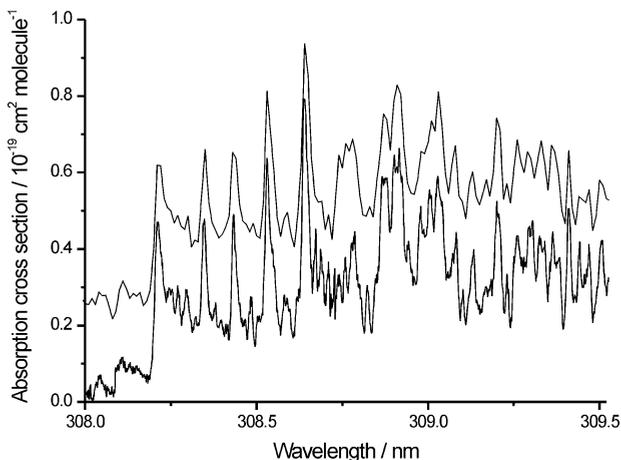
Fig. 2 Absorption spectra of formaldehyde in the air wavelength region 308–309.5 nm obtained at resolutions of 0.01 nm (grey line, offset vertically by 0.2×10^{-19} cm^2 molecule^{-1} for clarity) and <0.0016 nm (black line).

at longer wavelengths where the excited state lifetimes are likely to be longer (and thus spectral lines sharper) than the ~ 10 ps or less estimated for levels populated at excitation wavelengths from 300–320 nm.

The current understanding of the photochemistry of formaldehyde is that excitation to the S_1 state is followed by internal conversion (IC) to highly excited vibrational levels of the ground (S_0) electronic state, or intersystem crossing (ISC) to the T_1 state. The barrier to dissociation to $H_2 + CO$ on the S_0 potential energy surface (PES) corresponds to an excitation wavelength of ~ 360 nm, the $H + HCO$ channel opens up for wavelengths shorter than 330 nm, and dissociation to $H + HCO$ over a barrier on the T_1 PES has an energetic onset corresponding to wavelengths shorter than ~ 310 nm. Thus, for $\lambda < 310$ nm we expect competition between dissociation pathways to $H + HCO$ *via* the T_1 and S_0 PESs, with the additional likelihood of tunnelling through the T_1 state barrier at lower energies. We might therefore anticipate significant changes in the radical quantum yield at wavelengths shorter than ~ 310 nm as the T_1 route opens up, so one purpose of our most recent study was to investigate this possibility.

All the absorption bands of HCHO are rovibrationally structured, and thus will show temperature dependence to individual line intensities because of changing Boltzmann populations of S_0 rovibrational levels. Total $H + HCO$ yields, which depend on the product of the absorption cross-section and the quantum yield, should thus be temperature dependent at all excitation wavelengths. We have not yet conducted Stern–Volmer analysis of the pressure dependence of quantum yields because, for the bands studied so far, indications from our linewidth measurements are that the excited state lifetimes for HCHO are much shorter than the nanosecond lifetimes reported for acetone and other ketones.[1] We thus expect collisional quenching effects to be less significant.

1 E. W. G. Diau, C. Kötting and A. H. Zewail, *ChemPhysChem.*, 2001, **2**, 273 and references therein.

Dr Wang commented: We have recently measured the absolute HCO quantum yield from photolysis of glyoxal (HCOCOH) using the reaction with chlorine as the reference. Mixtures of glyoxal and chlorine, keeping glyoxal concentration constant while varying chlorine concentration, were photolyzed, and the HCO radical produced was detected using CRDS. At 308 nm, the quantum yield of chlorine atoms from photolysis of Cl_2 is 2. The chlorine atoms will react with HCOCOH, producing HCOCO radical, which will decompose to HCO + CO on a short time scale ($k > 10^7$ s).[1] The HCO from photolysis of the mixture is then proportional to $\phi_{Gly}\sigma_{Gly} + 2\sigma_{Gly}x_{Cl_2}/x_{Gly}$. With known absorption cross sections for glyoxal and Cl_2,[2] the absolute quantum yield is

determined as ~0.76, which agrees with previous values of 0.7 ± 0.3 by Zhu *et al*.[3] We would think this method is applicable to formaldehyde.

1 J. J. Orlando and G. S. Tyndall, *Int. J. Chem. Kinet.*, 2001, **33**, 149–156.
2 R. Volkamer, P. Spietz, J. Burrows and U. Platt, *J. Photochem. Photobiol. A*, in press; D. Maric, J. P. Burrows, R. Meller and G. K. Moortgat, *J. Photochem. Photobiol. A: Chem.*, 1993, **70**, 205–214.
3 Y. Chen and L. Zhu, *J. Phys. Chem. A*, 2003, **107**, 4632–4651.

Professor Orr-Ewing responded: The question of how to place relative quantum yield measurements for formaldehyde photolysis on an absolute scale is an important one, and the method suggested by Dr Wang is an interesting possibility. This approach could be used to determine absolute quantum yields at a few selected photolysis wavelengths, but is unlikely to be practical for high resolution determination of quantum yields over the wide spread of wavelengths relevant to tropospheric photochemistry. Our method of relative quantum yield determination is thus essential to map out the rapid variations of ϕ between the selected wavelengths used for absolute value measurements. It would be interesting to know whether the uncertainty associated with the quantum yield reported by Dr Wang for glyoxal improves significantly on the measurement of Chen and Zhu, and thus what precision might be expected for equivalent studies of formaldehyde. The possibility of secondary reactions of the HCO products will need to be considered carefully. We note that a precise absorption cross section for formaldehyde of the type we also measure in our apparatus, corrected if necessary for the bandwidth of the photolysis laser (which will be large for a 308 nm excimer laser), will be an important parameter in analysis of the suggested formaldehyde quantum yield measurements.

We have also given thought to putting our relative quantum yields onto an absolute scale that is independent of previous measurements, and envisage a strategy that does not rely on HCO detection, but that detects the photoproducts of the photolysis directly.

Professor Heard asked: Can you please elaborate on the "alternative experimental strategy that does not require knowledge of σ_{HCO} or the extent of overlap of the lasers, but which measures absolute radical channel yields at a few selected wavelengths" alluded to in your paper for the determination of absolute quantum yields for HCO?

Professor Orr-Ewing replied: Our intention is to measure a signal from H atoms produced by photolysis of a known partial pressure of HCHO at selected UV wavelengths, and compare that signal to the H atom signal from photolysis of a known pressure of HI under otherwise identical conditions. The wavelength dependent absorption cross sections for HI are well known and the quantum yield for production of H atoms is unity. Scaling the signals, with correction for the magnitudes of the HCHO and HI absorption cross sections, should give absolute quantum yields for H, and thus HCO production from HCHO photolysis.

Professor Duxbury asked: What ro-vibronic coupling method are you using for coupling between the probed and coupled states?

Professor Orr-Ewing said: The focus of our current studies of formaldehyde photochemistry is on the measurement of precise quantum yield and absorption cross section data of importance to atmospheric scientists, rather than detailed interpretation of the mechanisms for intersystem crossing and internal conversion that lead to dissociation of the S_1 state. Nevertheless, we are aware that our experimental data provide important information on the couplings between the S_1, S_0 and T_1 states, *via* perturbations in spectral line positions, line broadenings, and HCO yields. The mechanisms for the ro-vibronic coupling have been discussed in detail by Wittig and coworkers,[1] who studied the photodissociation dynamics of jet-cooled HCHO at energies in the vicinity of the barrier on the T_1 potential energy surface. Further work is currently being undertaken at Bristol by Miss B. Cronin and Prof. M. N. R. Ashfold, using H-atom photofragment translational spectroscopy, to unravel the complicated excited state dynamics of this molecule.

1 L. R. Valachovic, M. F. Tuchler, M. Dulligan, Th. Droz-Georget, M. Zyrianov, A. Kolessov, H. Reisler and C. Wittig, *J. Chem. Phys.*, 2000, **112**, 2752.

Professor Duxbury asked: What parallel is there between the Moore group work on ketene (similar symmetric structure) and formaldehyde?

Professor Orr-Ewing replied: There are some superficial parallels between the photochemistry of formaldehyde and ketene. For example, extensive work on ketene photochemistry by Moore and coworkers,[1] Ashfold and coworkers,[2] and others, shows that the primary dissociation routes for ketene, photoexcited to its S_1 or S_2 states, are *via* internal conversion or intersystem crossing to lower lying singlet and triplet states. As with HCHO, the T_1 state has a low barrier to dissociation (in the case of ketene, of height 1280 cm^{-1} relative to the zero-point energies of the $CH_2(\tilde{X}^3B_1)$ + CO photofragments). Beyond such general considerations, however, the value of comparisons ceases and a fuller understanding of the photochemistry of formaldehyde, which probably exhibits rovibrational level specific dissociation dynamics, requires a quantitative analysis of the rotational and vibrational energy levels of, and couplings between, the S_0, S_1 and T_1 states of the HCHO molecule itself.

1   E. A. Wade, H. Clauberg, S. K. Kim, A. Mellinger and C. B. Moore, *J. Phys. Chem. A*, 1997, **101**, 732.
2   E.J. Feltham, R. H. Qadiri, E. E. H. Cottrill, P. A. Cook, J. P. Cole, G. G. Balint-Kurti and M. N. R. Ashfold, *J. Chem. Phys.*, 2003, **6017**, 2003.

Professor Dibble commented: This work, even without absolute quantum yields for HCO, can be used to inform the work of Lei Zhu. She has measured HCO quantum yields from an extended series of linear aldehydes, in addition to the glyoxal molecule mentioned by Dr Wang. Dr Zhu has put her quantum yields on an absolute scale by comparison to quantum yields from H_2CO. Like you, she uses narrowband excitation of the aldehydes. Although their spectra lack the extensive structure seen in H_2CO, her normalization procedure could be improved by using the data you already have.

Professor Orr-Ewing replied: Dr Zhu has made a series of important measurements of HCO yields from aldehyde photochemistry using a photolysis and CRDS detection method similar to that described in our paper. If, as you suggest, our data for HCHO will be of value in refining the analysis of Dr Zhu's data, we will be happy to provide her with further details of our quantum yields.

Dr Taatjes asked: Could you remark on the possible sources of the observed pressure dependence of the HCO yield in the photolysis? Also, you mentioned in the paper that you are unable to investigate the HCO yield under realistic atmospheric conditions because of the rapid reaction of HCO with molecular oxygen. Have you considered whether measurement of the HO_2 product of this reaction (perhaps by absorption in the near-infrared) could offer a way to measure this yield in the presence of oxygen? The HO_2 radical should be long-lived under these conditions.

Professor Orr-Ewing replied: We can suggest two possible sources of the pressure dependence of the HCO yield, one of which relates to the properties of the molecule itself, and the other to the way in which we carry out the measurements. Testing these suggestions requires further experimental studies of the pressure dependence that we have not yet carried out.

The first possibility is that the addition of pressures in the region of 200 Torr of N_2 causes a broadening of structure within the pseudo-continua above the dissociation limits or barriers on the S_0 and T_1 potential energy surfaces. Rates of internal conversion and intersystem crossing from the S_1 state will depend in part on the energy overlap between the photoexcited rovibrational levels of the S_1 state and residual energy level structure in the S_0 and T_1 states. This structure might be broadened by collisions with N_2 molecules, reducing energy mismatches, and the effects are likely to be greater for the more sparsely structured region of energies in the vicinity of the barrier on the T_1 state.

The second, and perhaps more likely, explanation lies in the possible formation of rotationally and vibrationally excited HCO from HCHO photodissociation. Wittig and coworkers[1] demonstrated that the nascent HCO can be produced in excited K_a rotational levels, and a small

fraction is formed with a quantum of excitation of the bending vibration. Our laser based cavity ring-down detection scheme probes the HCO on the diffuse (0,8,0)–(0,0,0) vibrational band of the $\tilde{A}^2A''$–$\tilde{X}^2A'$ electronic transition, and thus is sensitive only to products in their zero-point vibrational level. The time delays used in our experiments should ensure rotationally thermalised HCO (as confirmed by spectra of the rotationally structured (0,9,0)–(0,0,0) band), but vibrational relaxation may be incomplete in the absence of the N_2 bath gas. What we observe may thus be the result of decay of bend-vibration excited HCO to the ground state when the bath gas is present.

Measurements of the effects of O_2 on radical quantum yields by detection of HO_2 radicals is an interesting but experimentally challenging suggestion. The HO_2 could, in principle, be monitored *via* its structured, but weak, near infra-red absorption features, or *via* its diffuse UV band system, using a sensitive technique such as CRDS.

1 L. R. Valachovic, M. F. Tuchler, M. Dulligan, Th. Droz-Georget, M. Zyrianov, A. Kolessov, H. Reisler and C. Wittig, *J. Chem. Phys.*, 2000, **112**, 2752.

Professor Ravishankara commented: It is wonderful to see your beautiful high resolution data on Φ (HCO) in formaldehyde photolysis. Congratulations! It would be useful if you took your data and yield over integrated wavelength bins that were measured earlier, for example the beautiful work of Moortgat. Measuring HCO *vs.* HOO yield in HDCO photolysis would be useful.

Dr Eisfeld opened the discussion of Dr Seakins's paper:
(1) DFT results must be interpreted with caution. In the entrance channel there are free unpaired electrons coupled to a doublet state. This situation cannot be treated by single-reference methods like DFT. In the calculation of the transition state to the exit channel, a concerted mechanism is enforced because a single bond breaking, forming three open shells, cannot be obtained by the applied method. For an unbiased study of the mechanism, application of multi-reference theories would be required.
(2) The deep well obtained after H-transfer indicates a lifetime of the intermediate which is sufficiently long to undergo the rapid association reaction with further O_2. Could this be an explanation for the observation that the yield of OH from $CH_3CH_2CO^{\bullet}$ is 30% higher than that from $CH_3CO^{\bullet}$? The quasi-steady-state situation means that $[O_2]$ must be in large excess.

Dr Seakins replied: Calculations here are only for reference. The highest level of our calculations is at the Gaussian-3 level, which should be reasonably accurate for reaction energetics and intermediates. The values for transition states at all levels are suspicious, due to large spin contamination in post-HF calculations. MRCI methods are better in principal, but are expensive and complicated in practice. In a ME/RRKM modelling, the actual barriers are often adjusted for a best fit to the experimental results.

The reaction path inferred from the PES is through TS1 to $CH_3CHC(O)OOH$ which will decompose. The chance to recombine with O_2 would be small. We observed no $[O_2]$-dependence in our OH yields.

Professor Zellner commented: We have recently completed a comprehensive experimental and theoretical study of the CO quantum yield in the photolysis of acetone at 248 nm.[1] In this work we found that the quantum yield of CO is pressure dependent with the quantum yield of CO changing from approximately 0.6 at 2 mbar to 0.25 at 700 mbar. Together with a combined quantum mechanical and RRKM dynamical calculation we show that this pressure dependence is caused by the competition between decomposition of internally excited acetyl radicals and their collisional stabilization.

The implication of this finding to the work presented here is that an additional pressure dependence is suggested to be necessary in the interpretation of the Stern–Volmer plots by invoking a competitive channel for RCO* radicals.

1 H. Somnitz, M. Fida, T. Ufer and R. Zellner, *Phys. Chem. Chem. Phys.*, submitted.

Dr Seakins replied: These are interesting observations and potentially very relevant for this work, although without access to the experimental data, it is difficult to comment specifically on these results.

We are aware that are results are made relative to a reference reaction and therefore that this reaction needs to be as well defined and characterised as possible. We believe that Figs. 4, 5b and the table of thermodynamic data on ketone photolysis provide sufficient evidence that the primary acetyl yield at 248 nm (photolysis energy = 482.5 kJ mol^{-1}) wavelength is not pressure dependent.

Fig. 4 in the paper shows that the pressure dependence of the kinetics of the OH yield is exactly the same with acetone, MVK and MEK as the ketone precursor, yet quite different for DEK. This suggests that acetone, MVK and MEK produce the same OH precursor, CH_3CO.

Photolysis of acetone, MEK and MVK releases 91, 133 and 71 kJ mol^{-1} into the acetyl and radical (CH_3, C_2H_5 and C_2H_3) co-product respectively. However, Fig. 5b of the paper shows that the yield of OH from each system has exactly the same pressure dependence despite the different reaction enthalpies of the photolysis processes. It seems unlikely, though not impossible, that such pressure dependence could arise if the acetyl fragment was subject to a further pressure dependence dissociation.

Professor Ravishankara addressed Professor Zellner: Could you 'reanalyse' Blitz *et al.*'s data with your measured $\Phi(CO)$ and $\Phi(CO_2)$ to see how much their quantum yields change?

Professor Zellner replied: Yes, in principle we could and certainly this might improve the general picture. However, we still do not see how this should improve the interpretation of the Blitz *et al.* data. In their experiments, hot acetyl radicals which we consider the major source of CO, are likely to escape detection.

Dr Blitz responded: You report that you have measured the CO yield for acetone photolysis at 248 nm. The CO yield was pressure dependent, with the quantum yield for $CO_2 + CO$ close to 1.0 at all pressures.

At Leeds we have demonstrated that the reaction $CH_3CO + O_2$ at low pressures produces OH, and recently in yet to be published work we have observed formaldehyde, which implies CO is also produced. However, the reaction $CH_3CO + O_2$ to $OH + CH_2O + CO$ switches to form peroxyacetyl, $CH_3CO(O_2)$, at higher pressures. My question: can this acetyl + O_2 reaction explain the observed CO pressure dependence in your acetone photolysis experiments?

Professor Zellner replied: The observation that $CH_3CO + O_2$ produces CH_2O (next to OH) is very interesting since it implies that CO might also be formed. Before this implication is applied to the current problem, the yield of CO in this reaction for different pressures must of course be quantified since otherwise there would be a permanent route from acetyl to CO at all low pressure conditions involving O_2. Whilst this is contradictory to at least some of the atmospheric observations, namely the formation of products such as PAN which can only be explained by acetylperoxy rather than CO formation, the potential of this reaction in our laboratory system should still be assessed. All our measurements were performed in pure N_2. However, even if we assume an O_2 impurity in the order of 100 ppm we estimate the first order rate coefficient for acetyl + O_2 to be between 10 to 10^3 s^{-1} depending on total pressure. In contrast the rate coefficient for the decomposition of hot acetyl radicals is several orders of magnitude larger. However, even if CO were produced from thermalized acetyl in its thermal decomposition ($k \sim 10$ s^{-1}, ref. 1), or by the reaction of acetyl with O_2 as suggested by Dr Blitz and Tyndall *et al.*[2] we do not consider these to be significant sources of CO except for low pressures (*i.e.* below 50 mbar). Hence we conclude that the reactions suggested by Dr Blitz are not significant contributors to the observed CO yields in our system and their respective pressure dependence. This applies in particular to the pressure effect observed above 50 mbar.

1 H. Somnitz, M. Fida, T. Ufer and R. Zellner, *Phys. Chem. Chem. Phys.*, submitted.
2 G. Tyndall, J. Orlando, T. Wallington and M. Hurley, *Int. J. Chem. Kinet.*, 1997, **29**, 655–663.
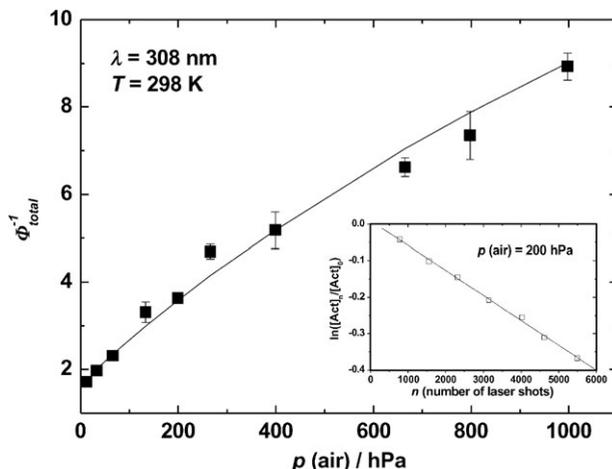
Fig. 3 Pressure dependence of the photodissociation quantum yield of acetone at $\lambda = 308$ nm and $T = 298$ K, in synthetic air. The filled squares are data from this study and the curve drawn is obtained from the parameterised quantum yield expression reported by Blitz et al.[1] ($\Phi_{total} = \Phi_{CH_3CO} + \Phi_{CO}$). The inset shows a representative plot from our experiments used to determine Φ_{total} at a given pressure.

Mr Kovács and **Professor Dóbé** communicated: This paper by Seakins et al. is a continuation of the detailed study of the Leeds group published very recently on the atmospheric photochemistry of acetone[1] by using their imaginative spectroscopic method to monitor the CH_3CO fragment in the form of OH by LIF. In the acetone work, Blitz and coworkers[1] have found the photodissociation quantum yield (QY) to be significantly smaller and to decrease with decreasing temperature at longer wavelength in contrast with previous determinations.[2,3] Arnold et al.[4] have applied the new QY values in a zero-dimensional photochemical box-model and concluded that acetone might play a significantly less important role in the chemistry of the troposphere than thought before. These recent findings have also been reviewed in comparison with the photolysis of the studied higher molecular weight ketones in the current work by Seakins et al. In an attempt to resolve the disparity that exists in the photodissociation quantum yields for acetone between the earlier determinations and the more recent ones, we have decided to undertake a comprehensive photochemical and photophysical study of acetone in relevance to atmospheric chemistry. Here we communicate our first results. The following reactions with the respective quantum yields as indicated are discussed below:

$$CH_3C(O)H_3 + h\nu \rightarrow products \qquad \Phi_{total}$$
$$CH_3C(O)H_3 + h\nu \rightarrow products \qquad \Phi_{CH_3CO}$$
$$CH_3C(O)H_3 + h\nu \rightarrow products \qquad \Phi_{CO}$$
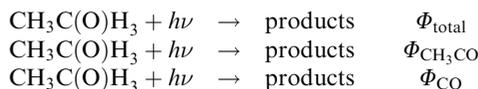
We have measured the quantum yield of acetone loss, Φ_{total}, by using pulsed laser photolysis (LP) coupled with gas-chromatographic analysis (GC). Our experimental method was very similar to that described by Gierczak et al.[2] The reactor was a quartz cylinder with Suprasil windows, surrounded by a thermostating jacket and equipped with a GC sampling port. The photolysis light was provided by an excimer laser. The GC parameters were: FID detection, 30 m quartz capillary column, HP-5 stationary phase, $T = 313$ K. The samples, containing 1.3 hPa acetone and varying amount of synthetic air, were irradiated with measured number of laser shots. The initial concentration of acetone and that remaining after n laser shots, respectively $[Act]_0$ and $[Act]_n$, were determined by GC analyses. Plotting of $\ln([Act]_n/[Act]_0)$ vs. n provided straight lines, from the slope of which Φ_{total} was obtained: $-\ln([Act]_n/[Act]_0) = \{\sigma(\lambda,T)\Phi_{total}(\lambda,p,T)F(\lambda)\}n$, where $\sigma(\lambda,T)$ is the absorption cross-section of acetone and $F(\lambda)$ is the laser fluence which was measured with a power meter calibrated by NO_2 actinometry (for further details see ref. 2). A typical example of such plots is shown in the inset of Fig. 3. Up to now we have performed experiments at 308 nm photolysis wavelength over a selected range of temperatures and pressures.

Table 1 Temperature dependence of the photodissociation quantum yield of acetone at $\lambda = 308$ nm in synthetic air

T/K	p(air)/hPa	$\Phi_{\text{total}} \pm 1\sigma$ This work[a]	$\Phi_{\text{CH}_3\text{CO}} + \Phi_{\text{CO}}$, ref. 1[b]
298	33	0.51 ± 0.03	0.50
273	33	0.41 ± 0.02	0.42
253	33	0.35 ± 0.04	0.36
233	33	0.31 ± 0.02	0.31
298	133	0.30 ± 0.02	0.34
273	133	0.24 ± 0.01	0.25
253	133	0.19 ± 0.02	0.20
233	133	0.12 ± 0.01	0.16

[a] LP/GC method to measure the photolytic loss of acetone. [b] Determination of CH_3CO quantum yields *via* LIF monitoring of OH formed as a minor product in the reaction of CH_3CO radical with O_2.

Table 1 summarises the quantum yields that we have determined at 298, 273, 253 and 233 K at two pressures. The data clearly show a decrease of Φ_{total} with decreasing T. Listed are also in Table 1 the quantum yields calculated by the parameterised $\Phi_{\text{CH}_3\text{CO}}$ and Φ_{CO} expressions reported by Blitz *et al.*[1] The agreement between the two sets of data is seen excellent contradicting with the previous recommendation of a temperature independent QY for the photodissociation of acetone under atmospherically relevant conditions.[2,3]

So far we have investigated the pressure dependence of Φ_{total} at room temperature. The results are presented in Stern–Volmer representation in Fig. 3. The data display a substantial pressure dependence and once again are in very good agreement with the prediction of the Leeds group.[1] Even the small curvature in the Stern–Volmer plot is reproduced by our data. This curvature, which is more pronounced at longer wavelengths,[1] may be taken as an indication that dissociation and quenching occur from more than one excited states of acetone. Lifetime and triplet quantum yield measurements have been underway in our laboratory in order to further clarify the photophysics of acetone.

The spectroscopic technique used in the Leeds studies is entirely different from our LP/GC method and so the good agreement in the quantum yields determined for the photodissociation of acetone is particularly comforting and lends credence for the reliability of this important photochemical parameter.

1   M. A. Blitz, D. E. Heard, M. J. Pilling, S. R. Arnold and M. P. Chipperfield, *Geophys. Res. Lett.*, 2004, **31**, L06111.
2   T. Gierczak, J. B. Burkholder, S. Bauerle and A. R. Ravishankara, *Chem. Phys.*, 1998, **231**, 229
3   IUPAC, *Evaluated Kinetic Data*, 2002, http://www.iupac-kinetic.ch.cam.ac.uk/.
4   S. R. Arnold, M. P. Chipperfield, M. A. Blitz, D. E. Heard and M. J. Pilling, *Geophys. Res. Lett.*, 2004, **31**, L07110.

Dr Taatjes asked Dr Seakins: I am interested in the possible products of the reactions of RCO radicals with O_2. Have you made any further calculations or performed any experiments to indicate, for example, the co-products of OH in the reaction of C_2H_5CO with O_2? Might ketene and formaldehyde be formed *via* the TS4 channel in Fig. 6 of your paper?

Dr Seakins replied: We too are interested in the mechanisms and products of these reactions, although we recognise that under most atmospheric conditions, their practical significance is low.

We have observed HCHO as a product of the acetyl + O_2 reaction, with the assumed co-products OH and CO. The analogous channel for the $C_2H_5CO + O_2$ reaction would be the formation of CO and acetaldehyde. We are currently developing a methodology for direct observation of CO by LIF through the B state, and acetaldehyde can be detected sensitively *via* GC.

The alternative pathway would generate a four-membered lactone which could be stabilised or, alternatively, fragment to either ketene + formaldehyde + OH or ethene + CO_2 + OH. The later channel is thermodynamically more stable. Direct observation of formaldehyde is possible

(although we may require indirect generation of the RCO radical as 248 nm DEK photolysis yields a radical species that absorbs and fluoresces in the HCHO observation region), the ethene/CO_2 channel would probably require GC detection of the ethene or possibly IR emission (CO_2).

Experiments on products from the $C_2H_5CO + O_2$ reaction are planned in the near future. Deuteration of the system may also shed light on the mechanisms.

Miss Farkas asked: How did you identify formaldehyde—the proposed co-product of OH formed in the reaction $CH_3CO + O_2$? Did you see its build-up concomitant with that of OH; what was the detection sensitivity?

Dr Blitz responded: Formaldehyde was probed by laser induced fluorescence at ~ 353 nm; its sensitivity for detection is $< 10^{10}$ molecule cm^{-3}. The trace below shows formaldehyde formation from the reaction between $CH_3CO + O_2$ at ~ 1 Torr total pressure. The bold line fit to the data yields a growth rate constant that is consistent with OH formation and a loss rate constant that is consistent with diffusion from the reaction zone.
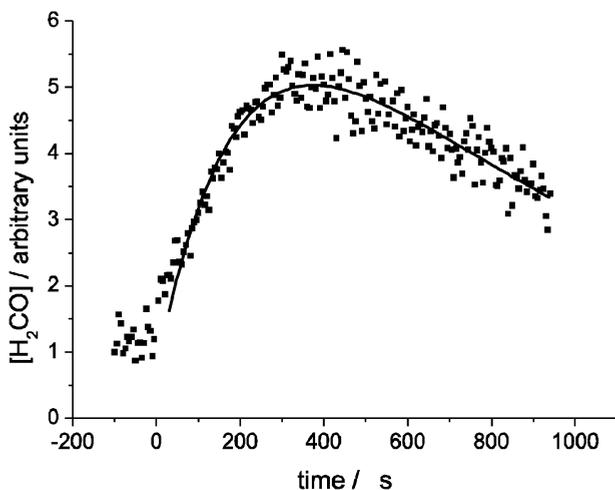
Professor Heard said: Prof. Zellner has referred to a measurement from his laboratory for the quantum yield of CO following photolysis of acetone at 248 nm.[1] In this work, the CO quantum yield at 248 nm is observed to be pressure dependent, which brings into question the assumption made by Blitz *et al.*[2] that the photodissociation quantum yield for acetone (*via* either of the thermodynamically available channels forming $CH_3CO + CH_3$ or $2\ CH_3 + CO$) is pressure independent at 248 nm. Has the temperature dependence of the CO yield at 248 nm (and any associated pressure dependent yields) been studied by Prof. Zellner's group?

1 H. Somnitz, M. Fida, T. Ufer and R. Zellner, *Phys. Chem. Chem. Phys.*, submitted.
2 M. A. Blitz, D. E. Heard, M. J. Pilling, S. R. Arnold and M. P. Chipperfield, *Geophys. Res. Lett.*, 2004, **31**, L06111, DOI: 10.1029/2003GL018793.

Professor Zellner replied: In the work of Somnitz *et al.*,[1] the temperature dependence of the CO quantum yield in the photolysis of acetone at 248 nm has not been studied. However, this dependence is the subject of a current investigation.

1 1 H. Somnitz, M. Fida, T. Ufer and R. Zellner, *Phys. Chem. Chem. Phys.*, submitted.

Dr Taatjes opened the discussion of Dr Sander's paper, which was presented by Dr Ingham: You have used the reaction of Br with Cl_2O_2 to show the dominance of the peroxide form, ClOOCl, of the ClO dimer. What limit do you place on the contribution of other isomers? Is the ionization energy of the other isomers known? A difference in ionization energy could be a means for

distinguishing the isomers in photoionization mass spectrometry measurements of ClO dimerization kinetics.

Dr Ingham replied: An upper limit of 10% was determined for (ClClO$_2$ + ClOClO) relative to ClOOCl. Our experiment was not designed to determine ionization energies as we were limited by the sensitivity of the mass spectrometer at low electron energies. This would have required much higher dimer concentrations than our pre-reactor could produce. The ionization energies of the three possible dimers have not been measured directly, but they have been estimated by *ab initio* calculations.[1] The calculated ionization energies of ClOOCl, ClClO$_2$, and ClOClO are 11.64, 10.95, and 10.11 eV, respectively. With a sufficiently intense and monochromatic photoionization source, mass spectrometry may well be a useful technique for the identification of the isomers.

1   M. Schwell, H.-W. Jochims, B. Wassermann, U. Rockland, R. Flesch and E. Ruehl, *J. Phys. Chem.*, 1996, **100**, 10070.

Dr Heard asked: Do any of the kinetic data presented in this paper change significantly any of the conclusions drawn when field-measured and model-calculated concentrations of the ClO dimer in the stratosphere are compared with one another?

Dr Ingham answered: These kinetic data do not have any impact on comparisons between field-measured and model-calculated concentrations of ClOOCl as the atomic concentrations are too low for these reactions to compete with ClOOCl photolysis. It is likely that OH + ClOOCl is more important and work is underway to measure the temperature dependent kinetics of this reaction.

Dr Cox asked a general question: Congratulations to the JPL Group on a very nice kinetics study. Any comment from the audience on the formation and decomposition of ClO dimer, a key reaction for polar ozone loss?

Dr Bloss replied: The kinetics of the ClO association reaction to form the ClO dimer, Cl$_2$O$_2$, were the subject of a recent study at the Jet Propulsion Laboratory (Bloss *et al.*[1]), with a particular focus upon the low pressure, low temperature regime relevant to the polar stratosphere, and upon the accuracy of the ClO absorption cross-sections used to derive the kinetic data. Prior to this work, the studies of Sander *et al.*[2] Nickolaisen *et al.*[3] and Trolier *et al.*[4] had obtained consistent values for the rate coefficient of the ClO self-reaction at higher temperatures ($T \geq 250$ K), but at lower temperatures, Trolier *et al.* reported a higher rate for the association reaction, by up to 26% (limiting low-pressure rate coefficient k_0 at 200 K). The recent JPL study[1] found that the discrepancies arose due to extrapolation at the lowest temperatures of the ClO absorption cross-sections used by Sander *et al.*; once this factor was taken into account, excellent agreement was obtained with the work of Trolier *et al.* Consequently our understanding of the kinetics of ClO dimer formation currently appears to be good; however there may still be uncertainties over (i) the isomeric identity of the Cl$_2$O$_2$ species formed, at the 10% level, and (ii) the equilibrium with/decomposition rate of the ClO dimer, which the JPL study of Bloss *et al.* did not address.

1   W. J. Bloss, S. L. Nickolaisen, R. J. Salawitch, R. R. Friedl and S. P. Sander, *J. Phys. Chem. A*, 2001, **105**, 11226.
2   S. P. Sander, R. R. Friedl and Y. L. Yung, *Science*, 1989, **145**, 1095.
3   S. L. Nickolaisen, R. R. Friedl and S. P. Sander, *J. Phys. Chem.*, 1994, **98**, 155.
4   M. Trolier, R. L. Mauldin III and A. R. Ravishankara, *J. Phys. Chem.*, 1990, **94**, 4896.

Dr Rowley said: In response to Drs Cox and Bloss, recent work in our laboratory supports the recent upward revision of the ClO + ClO association rate constant following the work of Bloss *et al.*, and further supports the previous studies of the thermodynamics of ClO association to form Cl$_2$O$_2$.[1] The thermal decomposition of Cl$_2$O$_2$ to two ClO radicals appears insignificant at stratospherically relevant temperatures. Thus whilst ClO association kinetics are now fairly well-established, perhaps the most important unresolved point is the nature of the ClO dimer. Dr Sander's paper finds no evidence for the existence of a ClO dimer other than the peroxide (ClOOCl) form and places a conservative upper limit of 10% of the ClO association forming ClClO$_2$ or

ClOClO. This is in keeping with previous experimental work on the nature of this molecule.[2] However, recent theoretical work has proposed a minor channel producing ClOClO in yields of up to 23% at 200 K and 100 Torr.[3] Depending upon the fate of this molecule, given the flux through the ClO self-reaction under ozone hole conditions, even a small branching fraction producing ClOClO could have a profound impact upon the rate of ozone loss through the ClO dimer cycle.

1   G. Boakes, PhD Thesis, University of London, 2003, manuscript in preparation.
2   M. Birk, R. R. Friedl, E. A. Cohen, H. M. Pickett and S. P. Sander, *J. Chem. Phys.*, 1989, **91**, 6588.
3   R. S. Zhu and M. C. Lin, *J. Chem. Phys.*, 2003, **118**, 4094.

Dr Cox responded: I look forward to publication of the new measurements of the ClO + ClO reaction. Experimental evidence both direct and indirect supports the ClOOCl structure for the ClO dimer. The existence of a bimolecular channel forming OClO + Cl implies significant formation of a ClOClO complex, but the overall channel to OClO has a barrier. Calculated well depths for XO + XO complexes have not hitherto offered unequivocal resolution of issues concerning the reaction kinetics. I would prefer to reserve judgement about formation and stability of the alternative structure.

Dr Ingham responded to Dr Rowley: Our results are not necessarily inconsistent with the theoretical calculations. We place an upper limit of 10% for ($ClClO_2$ + ClOClO) relative to ClOOCl at 25 Torr He, and if the channel forming ClOClO is more pressure dependent than that forming ClOOCl then one may expect to see enhanced ClOClO formation as the pressure is increased. This would be an interesting experiment to perform as more laboratory data are required in this area.

Professor Duxbury commented: Dr Sander's paper points out that the only spectrum (microwave) of the ClO dimer is of the peroxide. This is a "floppy" dimer whose binding energy can be inferred from the microwave spectrum. It should not be considered as a "rigid" peroxide.

Professor Wayne asked: Only the processes

$$Cl + ClOOCl \rightarrow ClOO + Cl_2$$
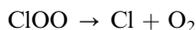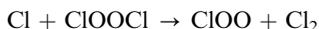
$$ClOO \rightarrow Cl + O_2$$

appear in your scheme for the species ClOO, and there are no alternative losses for ClOO. Every Cl lost in the first step reappears in the second. Your reaction between Cl and ClOOCl thus seems just to catalyse the recombination of Cl to Cl_2. Put another way, the processes are catalysis of the decomposition of ClOOCl to Cl_2 + O_2 and thus, ultimately, catalysis of the reaction

$$ClO + ClO \rightarrow Cl_2 + O_2$$
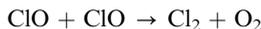
There are doubtless very high concentrations of ClO and ClOOCl in the rocket plume, but what impact does the reaction have on the chemistry occurring in such a plume? What is the anticipated change in [Cl]/[Cl_2] compared with the ratio if the reaction between Cl and ClOOCl did not occur? Are there any significant consequences that follow that would not arise were the process not to occur?

Dr Ingham replied: The reaction between Cl and ClOOCl does indeed catalyse the chain decomposition of ClOOCl to Cl_2 + O_2, but it also catalyses the destruction of O_3. Under solid rocket motor plume conditions the reaction does occur, and it is likely the rate limiting step in the propagation of the O_3 destruction cycle since it occurs much faster than the photolysis of ClOOCl (under normal sunlit polar stratospheric conditions the rate limiting step is ClOOCl photolysis). Impact is to increase the rate of O_3 loss over that where ClOOCl photolysis is rate limiting. One may expect that the local steady-state ratio [Cl]/[Cl_2] will be reduced, but it is beyond the scope of this work to provide a quantitative description of solid rocket motor plume chemistry. This would require modelling studies where factors such as chain termination *via* Cl + CH_4 and potential heterogeneous uptake of ClOOCl are considered.

Dr Kolb said: This high quality discharge flow reactor study demonstrates that radical/molecule reactions of Br, Cl, and NO with ClOOCl will not be major sinks for the high concentrations of ClOOCl in the exhaust plumes of solid fueled rockets that employ ammonium perchlorate as an oxidizer. Solid rocket motor using ammonium perchlorate as an oxidizer generally also use aluminum as a fuel, producing large numbers of α- and γ-alumina particles with diameters from ~ 0.02 to 10 μm.[1] Chlorine nitrate has been shown to react efficiently with HCl on alumina surfaces,[2] and this heterogeneous reaction has been predicted to be an important part of the long-term impact of solid-fueled rocket exhaust plumes on the atmosphere.[3] Atmospheric measurements and model analyses have also shown that adsorption of nitric acid vapor on alumina particles is an important sink for gaseous HNO_3 in stratospheric rocket exhaust plumes.[4] Laboratory studies have shown that alumina surfaces react with many chlorine containing compounds, even chlorofluoro-carbons.[5,6] These prior studies suggest that reactive heterogeneous uptake of ClOOCl on alumina particles may be an effective sink for this labile species in solid rocket motor plumes. The authors may want to examine this reaction in their flow reactor.

1   L. D. Strand, J. M. Bowyer, G. Varsi, E.G. Laue and R. Gauldin, *J. Spacecr. Rockets*, 2003, **18**, 297–305.
2   M. J. Molina, L. T. Molina, R. Zhang, R. F. Meads and D. D. Spencer, *Geophys. Res. Lett.*, 1997, **24**, 1619–1622.
3   M. Y. Danilin, R.-L. Shia, M. K. W. Ko, D. K. Weisenstein, N. D. Sze, J. J. Lamb, T. W. Smith, P. D. Lohn and M. J. Prather, *J. Geophys. Res.*, 2001, **106**, 12727–12738.
4   M. Y. Danilin, P. J. Popp, R. L. Herman, M. K. W. Ko, M. N. Ross, C. E. Kolb, D. W. Fahey, L. M. Avallone, D. W. Toohey, B. A. Ridley, O. Schmid, J. C. Wilson, D. G. Baumgardner, R. R. Friedl, T. L. Thompson and J. M. Reeves, *J. Geophys. Res.*, 2003, **108**(D4) 414, DOI: 10.1029/2002JD002061.
5   Q. Dai, G. N. Robinson and A. Freedman, *J. Phys. Chem. B*, 1997, **101**, 4940–4946.
6   G. N. Robinson, Q. Dai and A. Freedman, *J. Phys. Chem. B*, 1997, **101**, 4947–4953.

Dr Ingham responded: In rocket plumes the Cl + ClOOCl reaction acts as part of a catalytic ozone depletion mechanism in which the ClO dimer is regenerated. Dr Kolb correctly points out that a complete picture of rocket plume chemistry might include reactions involving ClOOCl that act as permanent sinks of active chlorine, such as heterogenous reactions of ClOOCl on alumina particles. In the conventional view, the major sink of chlorine will be the reaction of Cl with CH_4. For typical lower stratospheric concentrations of CH_4 ($\tilde{} 10^{12}$ cm^3 molecule^{-1} s^{-1} at 20 km altitude), the removal rate of chlorine is approximately 8×10^{-4} s^{-1}. Danilin *et al.* (ref. 4 above) find that the surface area density of particles in an Athena rocket plume range from approximately 400–1000 μm^2 cm^{-3}. Since the uptake of ClOOCl onto plume particles is given to first order by

$$d[\text{ClOOCl}]/dt = \text{SAD}(\gamma v_{\text{ClOOCl}}))/4$$

where SAD is the surface area density, γ is the uptake coefficient and v_{ClOOCl} is the mean thermal speed of ClOOCl, we estimate that the uptake coefficient for ClOOCl by alumina must be greater than $\tilde{} 10^{-2}$ in order for this process to compete with Cl + CH_4 for chlorine removal. A γ of this magnitude is certainly in the realm of possibility as similar uptake coefficients have been measured for HNO_3 on alumina. We agree with Dr Kolb that a study of ClOOCl uptake of alumina is warranted.

Professor Stephenson opened the discussion of Professor Hynes's paper: The paper by Hynes and co-workers highlights the importance of HOONO in modulating collision dynamics in the OH + NO_2 system. Recently, we have carried out investigations in the laboratory of Prof. Marsha Lester at the University of Pennsylvania that explore the spectroscopy and dynamics of HOONO that has been cooled in a supersonic free jet expansion.[1,2] Fig. 4 shows the energetics of this system, in which we illustrate that HOONO can adopt one of two conformers—the planar *cis–cis* configuration in which there exists an internal hydrogen bond, and the *trans–perp* configuration in which the heavy atoms lie approximately in the same plane, while the HOON dihedral angle is close to 90°.

To date, we have recorded the first and second infrared overtone spectra of *trans–perp* (*tp*) HOONO. These spectra are shown in Fig. 5. In the upper panel is the first overtone spectrum, with an origin of 6971.35 cm^{-1}. The fit to the rotational structure provides a precise determination of the structure of *tp*-HOONO, which is in agreement with *ab initio* electronic structure theory.[3] Homogeneous broadening of the ro-vibrational lines is observed; the corresponding lifetime of
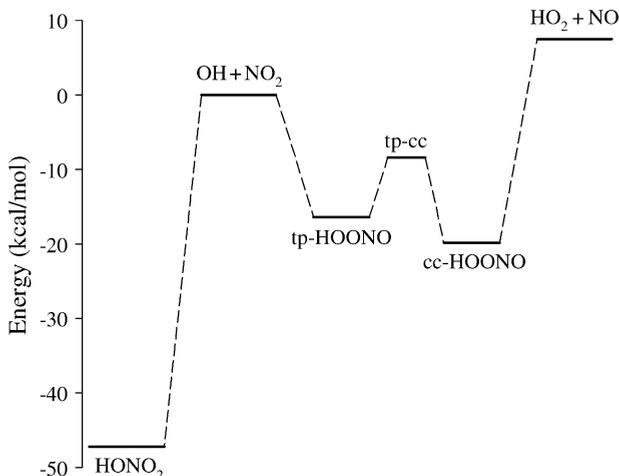
Fig. 4 Energetics of the OH + NO$_2$ system, showing the relative energies of nitric acid (HONO$_2$), the *cis–cis* (*cc*) conformer of HOONO and the *trans–perp* (*tp*) conformer of HOONO. The energy of the *trans–perp/cis–cis* isomerization barrier (*tp-cc*) is also shown.

the initially excited $2\nu_{OH}$ state is 27 ps.[1] In the lower panel of Fig. 5, the newly recorded second overtone spectrum of *tp*-HOONO is shown. The origin of this transition is 10 195.3 cm^{-1}, and the rotational band structure is consistent with the geometric parameters derived from the first overtone spectrum. Here the degree of homogeneous broadening is significantly higher, resulting in a lifetime of the $3\nu_{OH}$ state of 12 ps.[2]

Hynes and co-workers found that vibrational deactivation of OH by NO$_2$ results in a statistical distribution of OH products, *i.e.*, OH, $v = 0$ is the strongly favored product. Our investigations of the OH product distributions that result from the dissociation of *tp*-HOONO following $3\nu_{OH}$ excitation are consistent with this result. In Fig. 6, the OH $v = 0$ rotational distribution is shown, and compared with the results of a phase space theory calculation for the amount of excess energy available to products, 4530 cm^{-1}. The agreement is between theory and experiment is indicative of a statistical dissociation. Most relevant to the work of Hynes and co-workers is the vibrational branching that is observed between $v = 0$ and $v = 1$ OH. Vibrationally excited OH is a very minor product channel in the dissociation-so minor in fact that we are unable to quantitatively determine the branching ratio summed over all OH rotational, spin–orbit and Λ-doublet states. We are able to measure specific quantum state ratios. For example, we find that the ratio of population,

$$\frac{(v = 1, J = 2.5, \Omega = 1.5)}{(v = 0, J = 4.5, \Omega = 1.5)} = 0.036,$$

is close to the predictions of phase space theory (0.019) for this particular population ratio.[2]

These results illustrate the fruitful interplay between the photodissociation dynamics of weakly bound molecules such as HOONO and the collision dynamics of atmospherically relevant molecules.

1 I. M. Konen, I. B. Pollack, E. X. J. Li, M. I. Lester, M. E. Varner and J. F. Stanton, *J. Chem. Phys.*, 2005, **122** (9), 094320.
2 I. M. Konen, E. X. J. Li, T. A. Stephenson and M. I. Lester, *J. Chem. Phys.*, 2005, to be submitted.
3 B. D. Bean, A. K. Mollner, S. A. Nizkorodov, G. Nair, M. Okumura, S. P. Sander, K. A. Peterson and J. S. Francisco,
   J. Phys. Chem. A, 2003, **107** (36), 6974.

Professor Hynes replied: As we note in our paper the use of non-selective excitation for the production of vibrational excitation makes the technique vulnerable to systematic errors associated with cascading effects. The deactivation rates for OH ($v = 2,3$) measured using H$_2$O as a
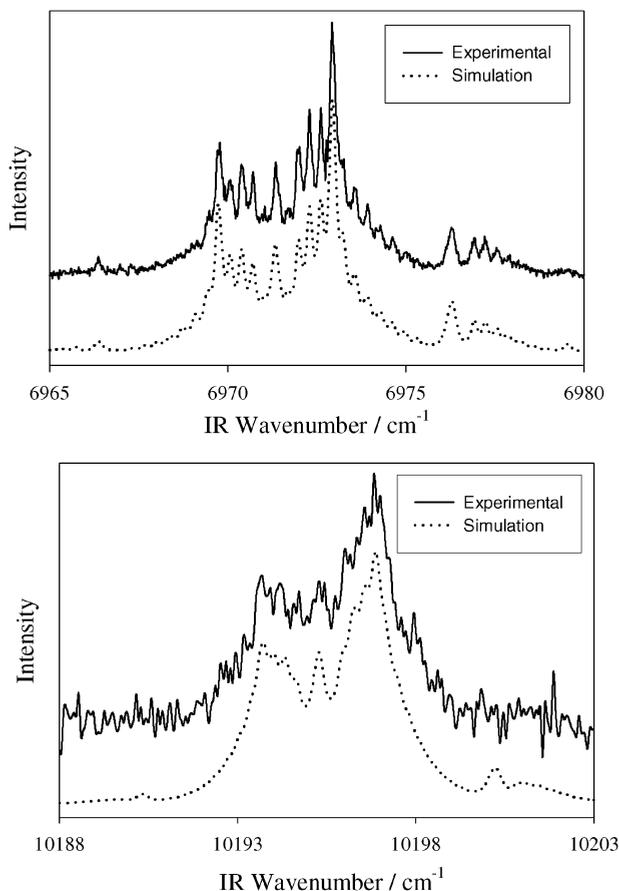
Fig. 5 Infrared overtone spectra of *tp*-HOONO with $2\nu_{OH}$ excitation (upper panel) and $3\nu_{OH}$ excitation (lower panel), along with spectral simulations.

precursor should not have any errors associated with cascading as OH is not produced with more than three quanta of vibrational excitation and production of OH ($v = 3$) appears to much smaller than OH ($v = 2$). The agreement between these rate coefficients and those measured using H_2 and CH_4 as precursors suggests that cascading errors are not significant using any of the OH (v) production schemes. The reactions of O^{1}D with H_2 and CH_4 produce more than 50% of the OH in levels with more than one quanta of vibrational excitation so measurements of deactivation of the $v = 1$ level are most susceptible to cascading errors. As we note in our paper deactivation by single quantum deactivation would produce a large error in the measured deactivation rate. However even a relatively small fraction, $\sim 10\%$, of deactivation proceeding *via* a single quantum process would produce an apparent decrease in the rate coefficient at the precision of our measurements. Nevertheless studies of these decay processes *via* direct excitation of single vibrational levels *via* OH overtone transitions would eliminate potential systematic errors associated with chemical production and cascading and offer the possibility of directly distinguishing the extent of single *versus* multiquantum deactivation. The very elegant studies reported by Prof. Stephenson go a step further directly producing the least stable of the three possible isomers with two quanta of vibrational excitation in the OH bond and demonstrating that OH ($v = 0$) is produced almost exclusively, in agreement with statistical expectations.
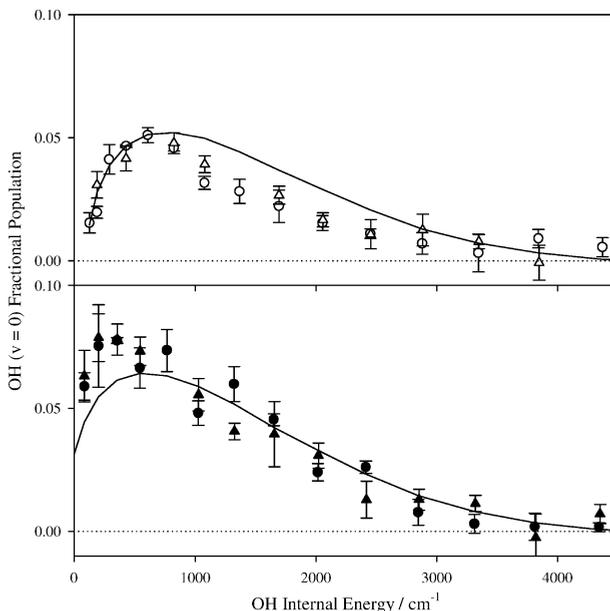
Fig. 6 OH, $v = 0$ product rotational state distributions that result from the second overtone ($3\nu_{OH}$) excitation of *tp*-HOONO. Solid symbols (lower panel) are the populations in the spin–orbit ground state ($\Omega = 3/2$). Open circles (upper panel) are the populations in the spin–orbit excited state ($\Omega = 1/2$). In both panels, the circles and triangles represent the A′ and A″ Λ-doublet states, respectively. The solid line is the prediction of phase space theory.

Professor Donahue asked: How rapid is interconversion of the two forms of HOONO (*cis–cis* and *trans–perp*) and what effect would this have on the bi-exponential OH decay data?

Professor Hynes responded: Based on the calculations of Golden *et al.*[1] the *trans*-isomer has a much faster decomposition rate than the *cis*-isomer but the *cis*-isomer accounts for greater than 95% of the total HOONO concentration. They report calculated isomerization rates for both isomers at 430 K and He pressures of 10^{20} and 10^{21} molecules cm^{-3}. At these pressures the isomerization rates are at least a factor of five faster than the unimolecular decomposition rates. However the isomerization rates are approaching the high pressure limit whereas the unimolecular decomposition rates are varying linearly with pressure. Consequently at the pressures used in our experiments we would expect the ratio of isomerization rate to decomposition rate to be even faster than at high pressures. Hence in both the high pressure experiments of Hippler *et al.*[2] and in this work we should observe biexponential decays which are averages of the decomposition rates weighted by the relative concentrations.

1   D. M. Golden, J. R. Barker and L. L. Lohr, *J. Phys. Chem. A*, 2003, **107**, 11057.
2   H. Hippler, S. Nasterlack and F. Striebel, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2959.

Professor I. W. M. Smith commented: The results reported by Prof. Hynes on the relaxation of vibrationally excited OH radicals are very interesting (and, to me, very gratifying). Of course, the rate of this relaxation serves as a good estimate of the rate of OH + NO$_2$ association in the limit of high pressure only when the rate constant (k_{diss}) for dissociation of OH(v)–NO$_2$ is much less than that for intramolecular vibrational redistribution (IVR) to OH($v' < v$)–NO$_2$. This seems very likely in this particular system where k_{diss} can be estimated as *ca.* 10^8 s^{-1} from the pressure dependence of the rate constant for the dissociation reaction: OH($v = 0$) + NO$_2$ → products (HNO$_3$ and HOONO$_2$).

My questions concern the conclusion presented in the paper that the products from the relaxation of OH($v \leq 5$) by NO$_2$ yields only OH($v = 0$) + NO$_2$. It seems to me intrinsically

unlikely that several quanta from the OH vibration are immediately and simultaneously transferred into other 'bath' modes in the complex. If these quanta are transferred sequentially, then one needs to ask whether partially relaxed complexes, *e.g.* OH(v − 1)–NO$_2$, will still be much slower than further IVR. So my questions are: (i) how certain can you be that multiquantum relaxation yielding OH(v = 0) + NO$_2$ is complete? and (ii) have you performed any RRKM calculations to estimate the rate constants for dissociation of the partially relaxed complexes?

Professor Hynes responded: If the loss of OH (v) occurs by deactivation, and the deactivation rate is equal for each OH (v) we can infer the absence of a significant fraction of the complexes dissociating to produce OH in $v > 0$ since this would produce measurement artifacts due to cascading. The question clearly relates to quantifying "significant". If deactivation occurs by a single quantum process then, as noted above, we would be sensitive to a 10% fraction of the energized complexes redissociating. However this figure depends on the assumed vibrational distribution of the OH produced in the reactions of O^{1}D with H$_2$ and CH$_4$. As we discussed in our recent work[1] on deactivation of OH (v) by O$_2$ and N$_2$, we appear to be the only group that has observed the production of OH (v = 5) in these reactions. For the OH (v) produced in reaction of O^{1}D with CH$_4$ we found good agreement with LIF excitation spectra when the relative populations of v = 3, 4 and 5 were taken to be 5 : 1 : 0.4 but these experiments were not careful attempts to extract internal state distributions. Certainly the small fraction of redissociation into $v > 0$ observed by Prof. Stephenson would not affect our results. We have not performed any RRKM calculations to estimate the rate constants for dissociation of the partially relaxed complexes. I would note that our observations on the rate of isotopic scrambling suggest that k_{diss} should be considerably faster that 10^8s^{-1}. Donahue *et al.*[2] estimated a dissociation rate of 8 × 10^8s^{-1} for the nitric acid complex and calculated that the isomerization rate of the ^{18}OH labeled nitric acid complex should be an order of magnitude faster. Our observations suggest that isomerization of labeled nitric acid and dissociation are occurring at competitive rates. Presumably the lifetimes of the HOONO complexes are even shorter. Nevertheless the lifetimes should still be on the scale of hundreds of vibrational periods of OH. In recent work Barker and coworkers[3,4] have used quasiclassical trajectory calculations to investigate intramolecular vibrational energy redistribution in nitric acid and the dynamics of the OH(v) + NO$_2$ reaction. They use an analytic potential energy surface that gives good agreement with the known structure and vibrational frequencies of nitric acid. The vibrational energy in the OH mode is monitored *via* the mean-square displacement of the bond length calculated during the trajectories. In their studies on OH(v) + NO$_2$ they find that the lifetime of the nascent excited HONO$_2$* depends strongly on its internal energy, but not to the extent predicted by statistical RRK theory. Lifetimes of complexes formed from OH (v = 5) are approximately a factor of ten shorter than those formed from the OH (v = 1) and vibrational deactivation is predicted to be approximately 90% efficient. However in spite of the difference in predicted complex lifetime, deactivation efficiency is almost independent of the initial vibrational state of the OH and deactivation of OH (v = 5) complexes is predicted to be slightly more efficient.

1   L. D'Ottone, D. Bauer, P. Campuzano-Jost, M. Fardy and A. J. Hynes, *Phys. Chem. Chem. Phys.*, 2004, **6**, 4276.
2   N. M. Donahue, R. Mohrschladt, T. J. Dransfield, J. G. Anderson and M. K. Dubey, *J. Phys. Chem. A*, 2001, **105**, 1515.
3   Y. Liu, L.L. Lohr and J. R. Barker, *J. Phys. Chem. B*, 2005, **109**, DOI: 10.1021.
4   Y. Liu, L. L. Lohr and J. R. Barker, *J. Phys. Chem. A*, submitted.

Dr Self said: It is important to know the rate constant k(OH = NO$_2$) under atmospheric conditions, with respect to the lifetime of OH in the atmosphere. It could account for part of the model *vs.* measurement discrepancy observed for the lifetime of OH.

Dr Cox replied: Concerning the current consensus on recommendations for the rate constant for the OH + NO$_2$ + M → products reaction, the IUPAC Evaluation Panel have updated and revised the preferred rate constant and comment on the formation of HOONO in http://www.iupac-kinetic.cam.ac.uk/.

Professor Donaldson addressed Professor Hynes: Your k_∞ value is based on the observation that all v-levels of OH($v = 1-5$) are found to be lost by collision with NO_2 at equal rates. To interpret this rate coefficient as the capture rate constant you model the expected result if these were to be deactivated *via* "cascade": $v = 5 \rightarrow v = 4 \rightarrow v = 3$ *etc*. Have you tested this model by measuring the OH(v) relaxation by CO_2 (for example), where complex formation is unlikely to occur, so vibrational relaxation may proceed in a "normal", single quantum manner?

Professor Hynes replied: As we discuss in our reply to Professor I. W. M. Smith, if the vibrational deactivation rates are identical and equal to the capture rate then vibrational deactivation cannot occur by single quantum deactivation unless currently accepted OH vibrational distributions for the precursor reactions are hugely in error. In previous work we have measured OH(v) relaxation where complex formation is unlikely to occur, so vibrational relaxation may proceed in a "normal", single quantum manner, specifically N_2, CH_4, and CH_3Br.[1,2] However in these cases the vibrational deactivation rate increases as a function of the vibrational excitation of the OH. If the deactivation rate increases by a factor of at least two for each addition quantum of vibrational excitation in the OH then cascading errors are small. This is the case for the three examples cited above and is likely to be the case for any non complex forming system at least at low OH (v). To test our "model" of single quantum deactivation we would require a system in which the vibrational deactivation rate has been measured and shown to be independent of the OH vibrational level and in which there is unlikely to be complex formation.

1   E. Silvente, R. C. Richter and A. J. Hynes, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2821.
2   L. D'Ottone, D. Bauer, P. Campuzano-Jost, M. Fardy and A. J. Hynes. *Phys. Chem. Chem. Phys.*, 2004, **6**, 4276.

Professor Heard asked: The $10 \pm 3\%$ yield of the weakly bound HOONO isomer obtained in this work compares favourably with the 7% yield calculated by Golden *et al*.[1] Poorer agreement with the recent calculations of Troe[2] and by Matheu and Green[3] is mentioned. What are the yields calculated by these two studies, and can you suggest a reason why they are significantly smaller than the calculations of Golden *et al*.?

1   D. M. Golden, J. R. Barker and L. L. Lohr, *J. Phys. Chem. A*, 2003, **107**, 11057.
2   J. Troe, *Int. J. Chem. Kinet.*, 2001, **33**, 878.
3   D. M. Matheu and W. H. Green, *Int. J. Chem. Kinet.*, 2000, **32**, 245

Professor Hynes replied: Troe[1] estimates, subject to many caveats, HOONO yields of 1.9% at 500 Torr in N_2 at 300 K with the suggestion that this should depend only weakly on temperature between 200 and 400 K. Matheu and Green[2] present two calculations for the rate coefficients for the nitric acid channel so their predicted HOONO yield at 350 Torr in He at 300 K is 2.4% in one case and 7.3% in the other. Troe presents a detailed discussion of the problems involved in the calculation of the rate coefficients for both the nitric acid and HOONO channels. He concludes that in these cases there is not sufficiently precise information on the potential energy surface and on intermolecular energy transfer to allow for reliable *a priori* prediction of rates. In this case theory is used to analyze the experimental database. The k_∞ for the nitric acid, for example, is based on a fit to the data of Dransfield *et al*.[3] In the work of Matheu and Green rate coefficients are calculated *a priori* however this only enables a calculation of the rate coefficient for the nitric acid channel to within a factor of three, with essentially lower and upper limits being calculated from different treatments of the coupling between the reaction coordinate and the external rotation of the excited complex. The more recent work of Golden *et al*.[4] is fit to the results of Hippler *et al*.[5] I think it is important for those in the atmospheric modeling community who need use these rate coefficients to recognize that while these calculations provide enormous insight into the basic physical chemistry of these association processes they cannot resolve relatively small discrepancies between experimental data. I think the current uncertainties in the association rate coefficient at atmospheric pressure and the branching ratio for isomer formation are small relative to the current predictive power of theory although they are very significant for atmospheric modeling purposes.

1   J. Troe, *Int. J. Chem. Kinet*, 2001, **33**, 878.

2   D. M. Matheu and W. H. Green, *Int. J. Chem. Kinet.*, 2000, **32**, 245.
3   T. J. Dransfield, K. K. Perkins, N. M. Donahue, J. G. Anderson, M. M. Sprenguether and K. L. Demerjian, *Geophys. Res. Lett.*, 1999, **26**, 687.
4   D. M. Golden, J. R. Barker and L. L. Lohr, *J. Phys. Chem. A*, 2003, **107**, 11057.
5   H. Hippler, S. Nasterlack and F. Striebel, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2959.

Professor Ravishankara asked: Have you considered the possibility that $OH(v'' = 5,4, \ldots) + NO_2$ can react to give $HO_2 + NO$?

Professor Hynes replied: We did not consider the possibility of reaction of OH (v) to give $HO_2 + NO$ which is a possibility for the excited HOONO complexes. The rate coefficients for isotopic scrambling show that isomerization of nitric acid complexes to form HOONO does not occur for the thermal reaction and I think it is unlikely to be significantly enhanced due to the vibrational excitation of OH. If this reaction were significant for HOONO complexes formed from the association of OH ($v = 5$–2) with NO_2 it would reduce but not eliminate systematic errors in the deactivation rate coefficients as a result of single quantum cascading. In the experiments described by Professor Stephenson, dissociation of the *tp*-HOONO to $HO_2 + NO$ would be exothermic for the second overtone excitation and the observations, I suspect, are consistent with dissociation to $OH + NO_2$ being the primary channel. RRKM theory would suggest that this is preferred channel by several orders of magnitude. Presumably, given the sensitivity of LIF detection of NO, the experiment could be used to confirm and quantify the presence of an $HO_2 + NO$ channel.